Investigation of Some Industrial Stabilizers for Rubbers and Selection of the Most Effective of Them

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At present the most widely spread classes of chemical compounds, which find application as stabilizers for rubbers, are phenols, amines, phosphites and thioesters. In this connection the antioxidant and antiozonant properties of nine best-quality industrial stabilizers of the phenol and amine type and their mixtures were studied. They were examined in the reactions of cumene initiated oxidation and ozonation in carbon tetrachloride solution, as well as by means of thermal, ozone and atmospheric degradation of rubbers without and after sample wash off by water.

The 77PD stabilizer exhibited the best complex properties and was found to be the most effective one. Efficient materials among the mixtures were those of 77PD and 4010NA with Flectol H or Santowhite crystals.

KEYWORDS: Industrial Stabilizers, rubbers, structure, properties, efficiency, diffusion

INTRODUCTION

Studies of rubber stabilizers, as well as the selection of the most effective of them, have received much attention in the recent years. The main reasons which make this research necessary are concerned with the duration of the useful life of the rubber products and the continuously growing environmental pollution. Protection of elastomers and rubbers, accomplished by adding small amounts of organic compounds (stabilizers), has already found wide application for several decades.[1]

A number of requirements are demanded of the stabilizers, however, practically they cannot be satisfied by a single compound. That is why the attention of many workers is directed to the design of mixtures of stabilizers which would meet the majority of these requirements[2] and, besides this, would manifest a synergistic effect.

The aim of the present work is to characterize and select the most effective stabilizers and mixtures of them and to offer the most powerful protective systems

to practice. A detailed study was carried out of the effect of oxygen and ozone both in liquid and solid phases.

EXPERIMENTAL

Stabilizers

The following stabilizers were used without further purification: 2,2'-methylene-bis-(4'-methyl-6-tert-butylphenol), Plastanox 2246, CY product (I); 2,2'-methylene-bis-(4-ethyl-6-tert-butylphenol), Plastanox 425, CY (II); 2,6-di-tert-butyl-4-methylphenol, Ionol, SH (III); N,N'-bis-(1,3-dimethylpentyl)-p-phenylenediamine, Satoflex 77, MO (IV); N-iso-propyl-N'-phenyl-p-phenylenediamine, 4010 NA, (V); phenyl-β-naphtylamine, Neozone D, DU (VI); 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline, Santoflex AW, MO (VII); 4,4'-thio-bis-(6-tert-butyl-m-cresol), Santowhite crystals, MO (VIII) and polymerized 1,2-dihydro-2,2,4-trimethylquinoline, Flectol H, MO. They were examined either separately by applying a 5×10^{-3} M concentration or as double mixtures of 2.5×10^{-3} M and 2.5×10^{-3} M concentrations.

Solvents

Carbon tetrachloride and cumene of p.a. purity grade were used in this work.

Elastomers

Several elastomers were applied to the present study, namely, synthetic polybutadiene rubber (SKD), USSR product, natural rubber (NK, Malaysia), stereoregular polyisoprene rubber (SKI-3, USSR), butadiene-styrene rubber (Bulex-1500, Bulgaria). They were used either without purification or after triple precipitation with ethanol from carbon tetrachloride.

Methods

(i) Inhibited oxidation of cumene in volumetric device.[3,4] The initiation was realized by a 5×10^{-2} M solution of azo-bis-(iso-butyronitrile), AIBN, at 343 K and the initiation rate (W_i) of 2×10^{-6} M $\times$ s^{-1}; (ii) Ozonation of stabilizers in carbon tetrachloride solution. A bubbling technique and spectral determination at $\lambda = 254$ nm of the ozone concentration at inlet and outlet of a 10 ml reactor were used;[5] (iii) Treatment of rubber samples by three independent techniques: thermal oxidation in a chamber (343 K, 20% elongation), ozonation in a chamber (3 ppm ozone concentration, 303 K, 20% elongation), and atmospheric degradation (March–October, 1982, 20% elongation). Also, the same techniques were used with samples washed off beforehand for 30 days. (iv) Evaluation of the physicomechanical parameters of the samples by a "Schopper" testing unit.

All the experiments were performed according to the Bulgarian and German (GDR) standards BDS-8851-77 and TGL-16890, respectively.

RESULTS AND DISCUSSION

Antioxidant properties

The effectivity of the stabilizers was estimated by the induction period (τ) and the coefficient of inhibition (μ).[3,4] Both parameters are defined by the equation:

$$\tau = \left(1 - \frac{\mu[\text{InH}]_0}{2e[\text{AIBN}]_0}\right)k_i^{-1} \tag{1}$$

where μ is determined by the W_i/W_{InH} ratio, $(W_{\text{InH}} = [\text{InH}]_0/\tau)$; e is the probability for the initiated radicals to leave the kinetic cage. This probability is commonly accepted to be equal to 0.6.[3] $[\text{InH}]_0$ is the initial concentration of the stabilizer (5×10^{-3} M or 2.5×10^{-3} M); $[\text{AIBN}]_0$ is the initial concentration of the initiator (5×10^{-2} M), and k_i is the rate constant of the AIBN decay at 343 K (3×10^{-5} s^{-1}).

If we substitute the above-mentioned values for e, $[\text{InH}]_0$, and $[\text{AIBN}]_0$ in Eq. (1) and accept the values of 1, 2, 3, and 4 for μ, the following respective values for τ are obtained: 44, 90, 142, and 200 for $[\text{InH}]_0 = 5 \times 10^{-3}$ M and 22, 43, 66, and 91 for $[\text{InH}]_0 = 2.5 \times 10^{-3}$ M. Experimentally observed values for τ of the individual stabilizers (I–IX) were 194, 123, 85, 97, 123, 41, 54, 126, and 66 respectively, for $[\text{InH}]_0 = 5 \times 10^{-3}$ M and values of 4.7, 3, 2, 2.3, 3, 1, 1.3, 3, and 1.6, respectively, were found for μ. Bearing in mind the structure of the stabilizer, it can be concluded that these values are reasonable.

Moreover, the reaction of cumene oxidation was used to examine mixtures of stabilizers (1:1) at concentrations of 2.5×10^{-3} M. Comparing the experimental values of τ with those estimated by means of Eq. (1) (Table I), one can see that the system Nos 1, 2, 3, 4, 5, 6, 8, 9, 10, 11, 13, and 14 exhibit a synergistic effect.

TABLE I

Induction periods of stabilizer mixtures in the reaction of cumene initiated oxidation

No. Stabilizer system	τ_{sum}[a] (min)	τ_{exp}[b] (min)	$\Delta\tau$
1 IV/I	134	242	+108
2 IV/II	109	115	+116
3 IV/III	86	119	+33
4 IV/VIII	109	205	+96
5 IV/IX	86	138	+52
6 V/I	157	93	−64
7 V/II	132	94	−38
8 V/III	109	154	+45
9 V/VIII	132	172	+40
10 V/IX	109	135	+26
11 VI/I	113	198	+85
12 VI/II	88	76	−12
13 VI/III	63	130	+65
14 VII/V	88	123	+35
15 VII/II	88	88	0

[a] Calculated by Eq. (1).
[b] Experimental value.

Further, we selected the systems Nos 1, 4, 5, 6, 9, and 10 for experiments with vulcanisats. This choice was justified by the strong synergism and by the reference data[1] on their antiozonant and antiflexcracking properties.

Standard samples (TGL-16890) from vulcanisats for sidewalls of pneumatic tyres, based on Bulex 1500, NR, and SKI-3 at the ratio of 50:20:30, were mixed with 3 phr of the systems selected above and treated by the techniques described in the Experimental (method (iii)). It was established that the tensile strength and relative extension of the samples after wash off upon the thermal degradation (21–28 days) with the individual stabilizers of the phenol type, I–III and VIII, were aggravated by 28 and 18%, respectively, whereas the amines, IV–VI and IX, showed an average of 6%. This can easily be explained bearing in mind the much more higher solubility of the phenols in water than that of the amines.[1] The same experiment with systems Nos 4 and 9 indicated that the above-mentioned parameters were decreased by 14 and 11%, respectively, while with the amines Nos 5 and 10, they were practically unchanged.

Upon degradation of vulcanisats under atmospheric conditions, the first cracks with systems 4, 5, and 9 were observed after 15 weeks while 11 weeks were sufficient for system 10. After wash off, in all cases cracks appeared within 8 weeks. By the end of the experiment, cracking with the unwashed systems 4, 5, and 9 was insignificant whereas about 120 surface cracks were observed with system 10. Washing off caused changes in the nature of cracking. A great number of cracks (about 120) of 1-mm depth were observed with systems 9 and 10 and only a very small number with systems 4 and 5.

Antiozonant properties

Rate constants of the interaction between a certain stabilizer and ozone were measured by means of ozonation in a solution of carbon tetrachloride. For this purpose changes of the ozone concentration at the inlet and outlet of a bubbling reactor were monitored. The rate constants with the phenols and amines were of the order of 10^4 and $10^6\, m^{-1} \times s^{-1}$, respectively. The order of the stoichiometric coefficients was between 1 and 2 with monophenols, 4-5 with thiobisphenol, 2-3 with monoamines, and 5–6 with paraphenylenediamine.

Samples of the investigated vulcanisats were parallelly exposed to ozone. Figure 1 shows the behaviour of the samples from the formation of the first crack till their complete destroying. As is seen, system 9 was the most resistant, systems Nos 4, 5, and 10 exhibited very good resistance whereas system 1 was unsatisfactory. The cracking picture was the following. A small number (40) of surface cracks were observed with systems 4 and 10, isolated cracks occurred with system No. 5, while a net of cracks was formed with system No. 9. After wash off the intervals of time for the appearance of the first crack practically were the same, however, the behaviour of the vulcanisats was different. A net of surface cracks was observed with Nos 9 and 10, separate cracks existed with system No. 5 and a few cracks could be found with system No. 4.

The effect of the investigated stabilizers was studied by using rubber solutions containing the stabilizing system No. 10 and reference solutions without this
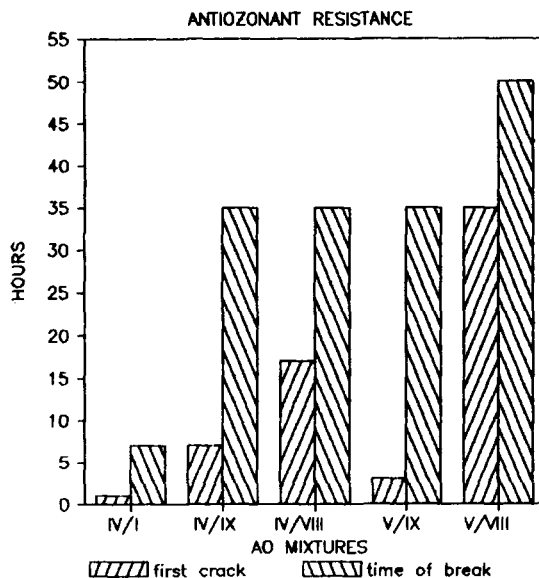
ANTIOZONANT RESISTANCE

FIGURE 1 Ozone degradation of the rubber samples in presence of systems Nos 1, 4, 5, 9, and 10 (3 ppm, 303 K, 20% elongation).

stabilizer. A bubbling reactor of 10-ml volume was loaded with a 5%-rubber solution mixed with such an amount of the stabilizing system that would correspond to 3 phr. An ozone-oxygen mixture of 1×10^{-4} M ozone concentration was passed through the reactor at the rate of $0.1 \text{ L} \times \text{min}^{-1}$.[5] The amount of consumed ozone was monitored spectrophotometrically at $\lambda = 254$ nm. The studied rubbers corresponded to those which were applied to the experiments mentioned above. The results are presented in Table II as stoichiometric coefficients.

It can be easily seen that the stabilizing system decreased the stoichiometric coefficient both with the technical grade rubbers and the purified ones. In all cases this is related to a lowering of the concentration of the reactive double

TABLE II

Stoichiometric coefficients of the ozone reaction with elastomers

No. elastomer	Purification	Stoichiometric coefficient	
		without No. 10	with No. 10
1 Bulex 1500	techn[a]	4	3
	pure[b]	2	<2
2 NR	techn	2	<2
	pure	1	~1
3 SKI-3	techn	2	1
	pure	1	<1
4 1:2:3 = 50:20:30	techn	3	1
	pure	1	<1

[a] Technical grade.
[b] Three-fold precipitated technical grade rubber.

bonds. Considering the technical grade rubbers, the change of concentration is also associated with the removal of unsaturated olygomers. Probably, the stoichiometry changes due to addition of a stabilizing system are consistent with deactivation of the double bonds by the stabilizer molecules, noting that one molecule of stabilizer deactivities from 2 to 4 double bonds. Bearing in mind the structure of stabilizers 5 and 9, we can imagine the formation of "associates" in which the double bond is screened by the stabilizers thus becoming inaccessible to further interaction. According to this conclusion, we take into consideration the actual concentrations (5×10^{-4} and 1×10^{-5} M) of rubber and stabilizer, respectively, as well as the rate constants of ozone with double C=C bonds (ca. $10^5\,M^{-1} \times s^{-1}$) and stabilizers (ca. $10^7\,M^{-1} \times s^{-1}$).[5] Nevertheless, this assumption appears to be only speculative. However, it is consistent with reported mechanisms which explain the antiozonant effect.[6]

Figure 2 shows the behaviour of these vulcanized samples in the presence of stabilizers IV and V. It is seen that, depending on the concentration, three zones of destroying, relative stability, and complete stability, respectively, can be assumed. These zones possess optimal parameters for 3 phr of stabilizer. Comparing these two stabilizers, it can be concluded that both are highly effective, however, the former one is slightly superior. This can be explained by the strong electronic properties of the ozone molecule. In all cases, the electron density of the reaction centres is hihger with IV due to the stronger electron-donor ability of the two alkyl substituents than that of the arylalkyl substituents.

It can be summarized that a detailed research is necessary to evaluate the effectiveness of the stabilizing systems, including: (i) invention of model conditions for a primary selection and presence of synergism; (ii) further selection
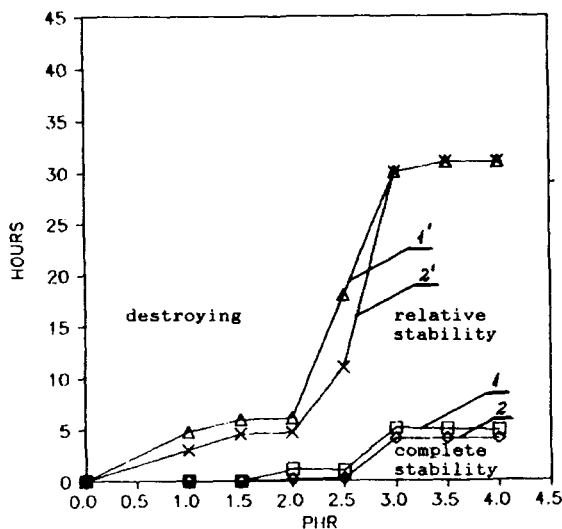

FIGURE 2   Ozone degradation of the rubber samples at various concentrations of stabilizers IV and V, curves 1,1' and 2,2', respectively (3 ppm, 303 K, 20% elongation, curves 1 and 2 are the first crack time and 1' and 2' are the time of brake).

by model experiments; and (iii) final selection of stabilizers examined under conditions used in practice. Simultaneous check of stabilizer effectiveness towards ozone, oxygen, heat, and light is appropriate at each stage of research. Light tests, however, are unnecessary with black vulcanisats. It was established that the following stabilizing systems were found to be the most effective: Nos 4, 5, 9, and 10 (Table I).

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